THE PHOTOINDUCED DEOXYGENATION REACTION OF HETEROCYCLIC N-OXIDES

Norisuke HATA, Isao ONO, and Masao KAWASAKI
Department of Chemistry, College of Science and Engineering,
Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo 157

The azanaphthalene N-oxides underwent the photochemical deoxygenation reaction in benzene containing BF_3-etherate, resulting in the formation of the parent amines in a 70-80% yield. The triplet sensitizations of quinoline-, isoquinoline-, and acridine-N-oxides by biacetyl or eosin also led to the dissociation of the N-O bond.

As is well known, the azanaphthalene N-oxides in solution isomerize upon irradiation of ultraviolet light to give lactams and/or oxazepines in a good yield, but the deoxygenation products (the parent amines) are formed only in a few percent yield.[1] On the other hand, it is also necessary to develop photochemical reactions leading to the formation of the parent amines in a high yield, since the deoxygenation reaction of heterocyclic N-oxides are of very importance in the syntheses of nitrogen heterocyclic compounds.[2]

It has been reported previously that the photochemical isomerization of isoquinoline N-oxide in water, as the pH of the solution was lowered (pH $<$ 0.3), became inefficient, while the quantum yield of the disappearance of N-oxide increased remarkably; this indicates that the protonated N-oxide undergoes photochemical conversions other than the isomerization.[3] In connection with this observation, Kaneko et al have found that the ultraviolet irradiation of 2-cyanoquinoline N-oxides in acidified alcohol resulted in the formation of 6-alkoxyquinoline-2-carbonitriles as a main product.[4] In view of these investigations, the irradiation of azanaphthalene N-oxides in the presence of Lewis acid appears to be interesting, because it may cause selectively the deoxygenation of N-oxides.

Therefore, the ultraviolet irradiations of azanaphthalene N-oxides listed in Table 1 were carried out in benzene containing BF_3-etherate. The general procedure of the photolytic experiment was as follows. A benzene solution (50 ml) containing 100 mg of N-oxide and 5 ml of BF_3-etherate in a Pyrex vessel was irradiated with a 100W high-pressure mercury immersion lamp (Riko Kagaku Sangyo Co.) for 1 or 2 hr under bubbling in of nitrogen. The irradiated solution was concentrated in vacuo and the concentrate was neutralized with a sodium carbonate aqueous solution. After the extraction with chloroform, the solution was concentrated under reduced pressure and subsequently chromatographed on a silica-gel or alumina column to separate the products. The product thus obtained was identified as the parent amine on the basis of UV spectrum and/or melting point determinations. As shown in Table 1, the yield of the deoxygenation product was 70-80% in all of the aza-

Table 1.   Photochemical Deoxygenation of Azanaphthalene N-Oxides

with BF_3-Etherate.

N-Oxide	Irradiation Time (hr)	Conversion (%)	Yield of Deoxygenation Product (%)
Isoquinoline N-Oxide	1	69	81
Quinoline N-Oxide	1	86	81
2-Phenylquinoline N-Oxide	2	100	69
3-Phenylquinoline N-Oxide	2	100	76
Quinaldine N-Oxide	2	100	82
Lepidine N-Oxide	2	100	83
4-Chloroquinoline N-Oxide	2	100	85
4-Bromoquinoline N-Oxide	2	100	78

Table 2.   Triplet Sensitized Deoxygenation of Aromatic Amine N-Oxides.

N-Oxide (E_T,kcal.mol^{-1})	Sensitizer (E_T,kcal.mol^{-1})	Solvent	Yield of Deoxygenation Product (%)
Quinoline N-Oxide (53.3)	Biacetyl (56.3)	Benzene	13
Isoquinoline N-Oxide (53.7)	Biacetyl (56.3)	Benzene	40
Acridine N-Oxide (37.2)	Eosin (40.3)	Ethanol	52

naphthalen N-oxides examined.   This novel photoinduced deoxygenation reaction could be applied for the synthetic means of nitrogen heterocycles, although the reaction mechanism is not clear at present.

Next, the triplet sensitized reactions of quinoline-, isoquinoline-, and acridine-N-oxides were carried out.   In a previous paper,[3] the triplet excitation energy of isoquinoline N-oxide has been determined from the phosphorescence maximum to be about 53.7 $kcal.mol^{-1}$, and the biacetyl-sensitization of isoquinoline N-oxide in deaerated methanol has been found to yield the isoquinoline in a 30% yield. Kubota et al have estimated the excitation energy of the lowest triplet state of non-phosphorescent quinoline- and acridine-N-oxides to be 53.3 $kcal.mol^{-1}$ and 37.2 $kcal.mol^{-1}$, respectively, by means of the oxygen-perturbed S-T absorption spectro-scopy[5]; that is, the biacetyl (E_T = 56.3 $kcal.mol^{-1}$) or eosin (E_T = 40.3 $kcal.mol^{-1}$) is expected to be usuable as a triplet sensitizer for the quinoline- or acridine-N-oxide.   Therefore, both the biacetyl-sensitization of quinoline- or isoquino-line-N-oxide in benzene and the eosin-sensitization of acridine N-oxide in ethanol were undertaken in nitrogen atmosphere.   The light source was 250W high-pressure mercury lamp (Ushio-250) equipped with a Toshiba filter VY-43 or V-O52. In the case of quinoline- or isoquinoline-N-oxide, a benzene solution (12 ml) containing 6.0 X 10^{-3}M of N-oxide and 1.5 X 10^{-2}M of biacetyl in a quartz cylindrical reaction vessel (4.5 cm in diameter and 0.8 cm in length) was irradiated with light longer than 430 nm for 10 hr.   Similarly, a solution of acridine N-oxide (2.0 X 10^{-3}M) and eosin (1.8 X 10^{-3}M) in   ethanol (70 ml) in a quartz cylindrical vessel (4.4 cm in diameter and 4.8 cm in length) was irradiated with light longer than 520 nm for 20 hr.   The photoproducts were then separated by silica-gel chromatography.   Consequently, as shown in Table 2, the dissociation of the N-O bond was induced to give rise the deoxygenation product; this definitely confirms the previous conclusion that the lowest π,π^* triplet state of the N-oxide[6] is responsible for the deoxygenation, but not for the isomerization.[3]

Furthermore, it is of interest that the lowest π,π^* triplet state responsible for the N-O bond cleavage has the excitation energy lower than the N-O bond energy (about 110 $kcal.mol^{-1}$).[7]   This could be accounted for by assuming that the dissociation of the N-O bond takes place from the lowest π,π^* triplet state in a predissociative manner (a crossing-over of the π,π^* triplet excited molecule to the repulsive σ,σ^* triplet localized in the N-O bond), just as in the case of the photolysis of pyridine N-oxide vapor.[7]

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